

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A61K 7/00		A2	(11) International Publication Number: WO 99/48462 (43) International Publication Date: 30 September 1999 (30.09.99)
(21) International Application Number: PCT/EP99/01632			(72) Inventors: ASHTON, Melanie, Ruth; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). GRIFFITHS, Llyr, Glyndwr, Elida Fabergé, Usine et Laboratoires de Compiègne, ZI - Boîte postale 139, F-60881 Le Meux (FR). MORETTA, Anthony; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside, L63 3JW (GB).
(22) International Filing Date: 12 March 1999 (12.03.99)			(74) Agent: GRIFFITHS, Sarah, Helen; Unilever PLC, Patent Dept., Colworth House, Sharnbrook, Bedford MK44 1LQ (GB).
(30) Priority Data: 9806295.3 24 March 1998 (24.03.98) GB			(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).			Published <i>Without international search report and to be republished upon receipt of that report.</i>
(71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).			
(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).			
(54) Title: AEROSOL HAIRSPRAY COMPOSITION			
(57) Abstract A single phase autophobic hairspray composition comprising: a) from 0.5 % to 10 % by weight of a film-forming hairspray resin; b) from 10 to 60 % by weight of a propellant including a mixture of at least one hydrocarbon and a di(C ₁ –C ₄ alkyl) ether in a weight ratio from 5:1 to 1:10; c) from 0.01 % to 1.0 % by weight of an autophobic hairspray additive, being a surfactant or polymer which imparts autophobic behaviour to the hairspray composition, and d) water.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece			TR	Turkey
BG	Bulgaria	HU	Hungary	ML	Mali	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MN	Mongolia	UA	Ukraine
BR	Brazil	IL	Israel	MR	Mauritania	UG	Uganda
BY	Belarus	IS	Iceland	MW	Malawi	US	United States of America
CA	Canada	IT	Italy	MX	Mexico	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NE	Niger	VN	Viet Nam
CG	Congo	KE	Kenya	NL	Netherlands	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NO	Norway	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	NZ	New Zealand		
CM	Cameroon	KR	Republic of Korea	PL	Poland		
CN	China	KZ	Kazakhstan	PT	Portugal		
CU	Cuba	LC	Saint Lucia	RO	Romania		
CZ	Czech Republic	LI	Liechtenstein	RU	Russian Federation		
DE	Germany	LK	Sri Lanka	SD	Sudan		
DK	Denmark	LR	Liberia	SE	Sweden		
EE	Estonia			SG	Singapore		

AEROSOL HAIRSPRAY COMPOSITION

5

FIELD OF THE INVENTION

The invention relates to an aerosol hairspray composition to achieve styling with improved sensory attributes at high 10 water levels.

BACKGROUND AND PRIOR ART

15 Hairspray compositions must meet a number of functional requirements. These include good holding ability and curl retention without giving a harsh, brittle feeling to the hair.

20 Conventional hairspray formulations are ethanol based and therefore form highly wetting systems for hair. Coalescence of the aerosol droplets on the hair fibre and subsequent ethanol evaporation to leave solid polymer residue leads to a network of fibre-fibre bonds.

25 There are, however, undesirable consequences in coating hair with polymer, manifesting in perceptions of sensory negatives such as stiffness, rigid feel, stickiness or unnatural feel.

30 US 4,871,529 describes ethanol solvent-based hairspray compositions which employ a specific type of silicone copolyol which causes the hairspray composition to contract upon drying. This is described as an "autophobic effect" 35 which causes large droplets of the composition to form, and

produce larger juncture points between fibres. Localisation of deposits in this way is advantageous since it offers stronger bonds and more durable hold, yet reduced sensory negatives such as stiffness and unnatural feel.

5

US 4,871,529 advises the minimum amount of water in its autophobic systems, if water is present at all. Increasingly, however, with the advent of legislation concerning the volatile organic content of hairsprays, it is 10 desirable to formulate systems with relatively high water content.

10

15

U.S. Patent 5,021,238 (Martino et al.) reports the advance of using dimethyl ether (DME) as a hairspray propellant. DME allows use of water as the only solvent thereby significantly reducing the volatiles problem.

20

However, with this type of propellant it has proved impossible to achieve an autophobic effect at high water levels.

25

30

Alternatively, replacement of chlorofluorocarbons with hydrocarbon propellants has been discussed in U.S. Patent 4,859,455 (Nowak, Jr. et al).

However, a problem with hydrocarbon propellants is that it becomes impossible to achieve a single phase system at high water levels. For example, in a water-hydrocarbon system containing more than 15% hydrocarbon, the composition separates into two phases - an aqueous phase and a hydrocarbon phase.

35

We have now found that achievement of both an autophobic effect and a single phase system is possible through use of a specific mixture of propellants in combination with a

film-forming hairspray resin and an autophobic hairspray additive. Moreover the autophobic effect thus achieved is tolerant to high water levels.

5

SUMMARY OF THE INVENTION

10 The invention provides a single phase autophobic hairspray composition comprising:

- a) from 0.5 % to 10 % by weight of a film-forming hairspray resin;
- 15 b) from 10 to 60% by weight of a propellant including a mixture of at least one hydrocarbon and a di(C₁-C₄ alkyl) ether in a weight ratio from 5:1 to 1:10;
- 20 c) from 0.01% to 1.0% by weight of an autophobic hairspray additive, being a surfactant or polymer which imparts autophobic behaviour to the hairspray composition, and
- d) water.

25

DETAILED DESCRIPTION OF THE INVENTION

30 Film-Forming Hairspray Resin

35 The hairspray resins employed in compositions of the present invention should be capable of forming a film and holding the hair of the user in place after evaporation of the volatile components of the hairspray composition.

Hairspray resins are well known articles of commerce and many such resinous polymers are available commercially which contain moieties which render the polymers cationic, anionic, amphoteric or nonionic in nature. To provide optimum sprayability, the polymers employed in hairspray compositions typically range in number average molecular weight of from 5,000 to 100,000 with 10,000 to 50,000 being more preferred.

The amount of the resin may range from 0.5 to 10%, preferably 0.75 to 6% by weight of the total composition.

Examples of anionic hairspray resins are:

copolymers of vinyl acetate and crotonic acid;

terpolymers of vinyl acetate, crotonic acid and a vinyl ester of an alpha-branched saturated aliphatic 20 monocarboxylic acid such as vinyl neodecanoate;

copolymers of methyl vinyl ether and maleic anhydride (molar ratio about 1:1) wherein such copolymers are 50% esterified with a saturated alcohol containing from 1 to 4 carbon atoms 25 such as ethanol or butanol;

acrylic copolymers, terpolymers, etc., containing acrylic acid or methacrylic acid as the anionic radical-containing moiety with other monomers such as: esters of acrylic or methacrylic acid with one or more saturated alcohols having from 1 to 22 carbon atoms (such as methyl methacrylate, ethyl acrylate, ethyl methacrylate, n-butyl acrylate, t-butyl acrylate, t-butyl methacrylate, n-butyl methacrylate, n-hexyl acrylate, n-octyl acrylate, lauryl methacrylate and behenyl acrylate); glycols having from 1 to 6 carbon atoms 35

(such as hydroxypropyl methacrylate and hydroxyethyl acrylate); styrene; vinyl caprolactam; vinyl acetate, acrylamide; alkyl acrylamides and methacrylamides having 1 to 8 carbon atoms in the alkyl group (such as 5 methacrylamide, t-butyl acrylamide and n-octyl acrylamide), and other compatible unsaturated monomers. The polymer may also contain grafted silicone, such as polydimethylsiloxane.

One specific example of a suitable anionic hairspray resin 10 is the emulsion polymerised terpolymer of methacrylic acid, n-butyl acrylate and ethyl acrylate (e.g. in a weight percent ratio of 31:42:27, respectively). Another specific example is Ultrahold® 8 (CTFA-Cosmetic, Toiletries and 15 Fragrance Association designation of Acrylate/Acrylamide Copolymer).

Other suitable anionic hairspray resins include carboxylated polyurethanes. Carboxylated polyurethane resins are linear, hydroxyl-terminated copolymers having pendant carboxyl 20 groups. They may be ethoxylated and/or propoxylated at least at one terminal end. The carboxyl group can be a carboxylic acid group or an ester group, wherein the alkyl moiety of the ester group contains one to three carbon atoms. The carboxylated polyurethane resin can also be a 25 copolymer of polyvinylpyrrolidone and a polyurethane, having a CTFA designation PVP/polycarbamyl polyglycol ester. Suitable carboxylated polyurethane resins are disclosed in EP 0 619 111 A1 and US Patent No. 5,000,955. Other suitable hydrophilic polyurethanes are disclosed in US Patent Nos. 30 3,822,238; 4,156,066; 4,156,067; 4,255,550; and 4,743,673.

Amphoteric polymers which can contain cationic groups derived from monomers such as t-butyl aminoethyl methacrylate as well as carboxyl groups derived from

monomers such as acrylic acid or methacrylic acid can also be used in the present invention. One specific example of an amphoteric hairspray resin is Amphomer® (octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer) sold by the National Starch and Chemical Corporation.

Examples of nonionic hairspray resins are homopolymers of N-vinylpyrrolidone and copolymers of N-vinylpyrrolidone with compatible nonionic monomers such as vinyl acetate and terpolymers of ethyl acrylate, butyl methacrylate and methyl methacrylate. Nonionic polymers containing N-vinylpyrrolidone in various weight average molecular weights are available commercially from ISP Corporation such as homopolymers of N-vinylpyrrolidone having an average molecular weight of about 630,000 sold by ISP (formerly GAF Corporation) under the tradename PVP K-90 and those having an average molecular weight of about 1,000,000 sold under the trademark of PVP K-120.

Examples of cationic hairspray resins are copolymers of amino-functional acrylate monomers such as lower alkyl aminoalkyl acrylate or methacrylate monomers such as dimethylaminoethyl methacrylate with compatible monomers such as N-vinylpyrrolidone, vinyl caprolactam, or alkyl methacrylates such as methyl methacrylate and ethyl methacrylate and alkyl acrylates such as ethyl acrylate and n-butyl acrylate.

Cationic resins containing N-vinylpyrrolidone are commercially available from ISP Corporation such as those sold under the trademarks of Copolymer 845 and Copolymer 937 (copolymers of N-vinylpyrrolidone and t-butylaminoethyl methacrylate of average molecular weight about 1,000,000) and Gafquat® 755 and 755N (quaternary ammonium polymers

formed by the reaction of dimethyl sulfate and a copolymer of N-vinylpyrrolidone and dimethylaminoethyl methacrylate of average molecular weight about 1,000,000).

5 With certain of the resins it may be necessary to neutralise some acidic groups to promote solubility/dispersibility. Examples of suitable neutralising agents include 2-amino-2-methyl-1, 3-propanediol (AMPD); 2-amino-2-ethyl-1,3-propanediol (AEPD); 2-amino-2-methyl-1-propanol (AMP); 2-amino-1-butanol (AB); monoethanolamine (MEA); diethanolamine (DEA); triethanolamine (TEA); monoisopropanolamine (MIPA); diisopropanol-amine (DIPA); triisopropanolamine (TIPA); and dimethyl stearamine (DMS). A long chain amine neutralising agent such as lauramidopropyl dimethylamine may be employed, 10 as is described in US 4,874,604. Mixtures of any of the above neutralising agents may be used. Amounts of the neutralising agents will range from about 0.001 to about 10% by weight of the total composition.

20

Propellant

Essential to the present invention is a mixed propellant system of hydrocarbon and dialkyl ether. The dialkyl ether 25 is a di(C₁-C₄ alkyl) ether, most preferably dimethyl ether. The hydrocarbon component of the propellant system will be a C₃-C₅ alkane, especially one selected from propane, isobutane, n-butane and mixtures thereof. An example is a combination of propane and isobutane, such as A50 propellant 30 commercially available from the Aeropress Corporation.

Total amount of propellant will range from 3 to 50%, preferably from 5 to 45%, optimally from 25 to 45% by weight of the total composition.

35

Weight ratios of total hydrocarbon to dialkyl ether will range from 5:1 to 1:10, preferably from 2:1 to 1:5, more preferably from 1:1 to 1:4, optimally about 1:2 by weight.

5

Autophobic Hairspray Additive

Also essential to the present invention is an autophobic hairspray additive, being a surfactant or polymer which 10 imparts autophobic behaviour to the hairspray composition.

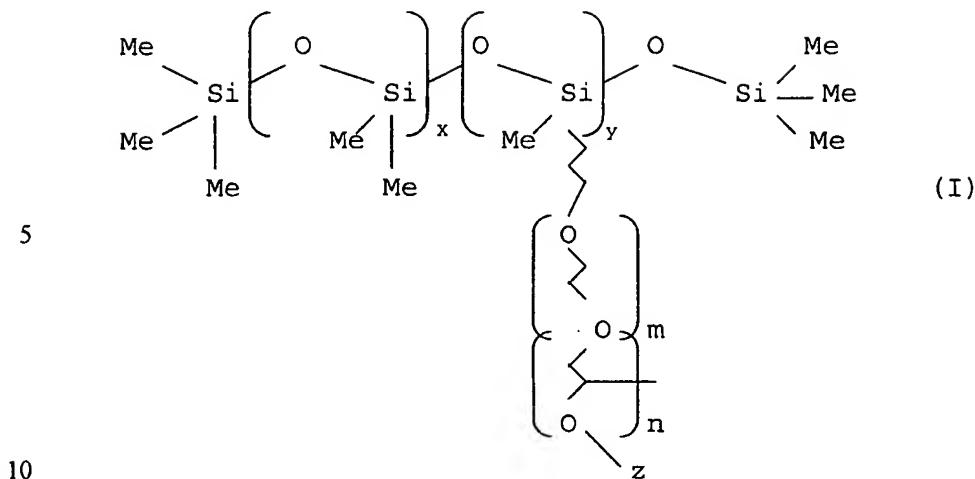
Autophobic behaviour of the hairspray composition can conveniently be evaluated as follows:

15 Conventional systems display high wetting of hair fibres. In these systems, solid (including hairspray resin) deposited in fibre-fibre junctions is significantly spread along the fibres from the centre of the junction along the length of the fibres. In contrast, autophobic systems 20 appear to localise deposition at fibre-fibre junctions, with a reduced coating of those fibre regions external to the junctions. This is consistent with the deposit being formed from a poorly wetting system, that is, the liquid makes a high contact angle with the fibre. The high contact angle 25 droplet morphology of the dried autophobic system on crossed hair fibres can be viewed by magnifying lens.

30 Suitable autophobic hairspray additives may be selected from the group consisting of:

(i) alkyl-pendant silicone copolyols of formula (I):

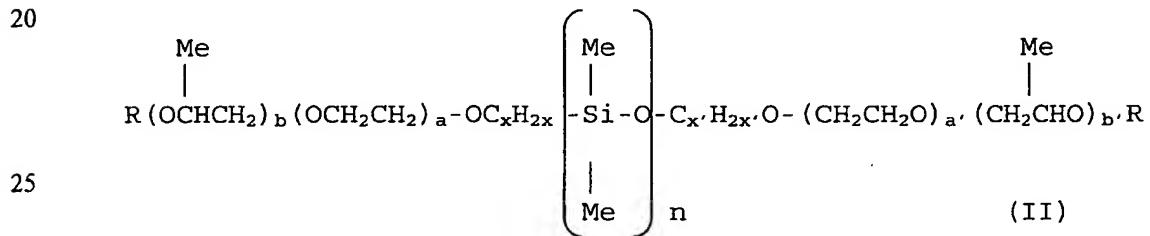
9



where m and n are integers of from 0 to 50, and x and y are integers chosen to give the copolyol a molecular weight of at least 600. Z is hydrogen or a C1-4 alkyl radical;

15

(ii) dimethicone copolyols of formula (II):

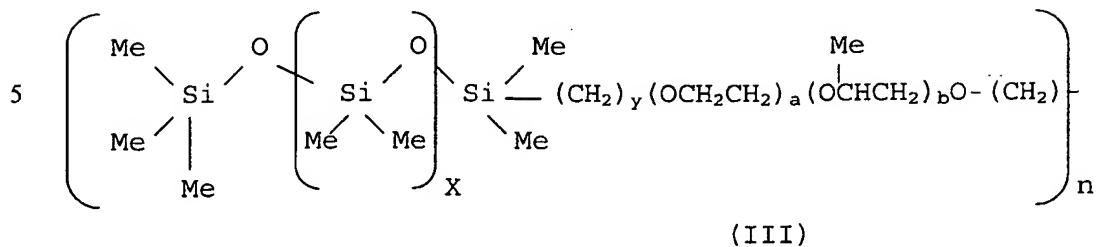


30

where n is an integer chosen to give the copolyol a molecular weight of at least 600; x and x' are integers of from 1 to 12; a, a', b, b' are integers of from 0 to 50, and R is hydrogen or a C1-4 alkyl radical;

35

(iii) polydimethicone copolyols of formula (III):



10

where x and n are integers chosen to give the copolyol a molecular weight of at least 500;
 y is an integer of from 1 to 12, and
 a and b are integers of from 0 to 50;

15

(iv) alkyl ethoxylates; and

(v) fluorosurfactants.

20 Illustrative alkyl-pendant silicone copolyols of formula (I) as referred to above are described in US 4,871,529. A preferred example is the ethoxylated dimethicone copolyol SILWET® L-7602, ex OSI Specialties.

25 Dimethicone copolyols of formula (II) referred to above are sometimes designated as "ABA" type copolymers, due to the presence of alternating polyalkylene oxide and silicone blocks.

30 Polydimethicone copolyols of formula (III) referred to above are sometimes designated as (AB)_n type copolymers.

The molecular weight of the copolyols of formulae (II) and (III) suitably ranges from 500 to 50,000.

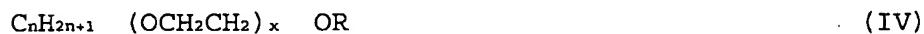
35

Suitable dimethicone copolyols of formula (II) are SILSOFT®900, sold by OSi Specialties, having a molecular weight of about 2000, with R being hydrogen and a being 0, and the materials sold by Goldschmidt as TEGOPREN® 3012 and 5 5830 respectively.

Suitable polydimethicone copolyols of formula (III) are those described in US 4,242,466. Illustrative is the 10 material sold by OSi Specialties as SILSOFT® 487, having a molecular weight of about 150,000, with a and b both greater than 0.

Examples of suitable alkyl ethoxylates are those of general formula (IV) :

15



where n is an integer of from 5 to 20, preferably from 8 to 20 18, most preferably 12 to 14;

x is an integer of from 3 to 50, preferably from 3 to 30; and

25 R is hydrogen or a C₁₋₄ alkyl group, e.g. methyl. Preferably R is hydrogen.

Illustrative are GENAPOL® C-250, (ex Hoechst Celanese), which is coconut fatty alcohol (C₈-C₁₈, mainly C₁₂-C₁₄) 30 ethoxylated with 25 moles of ethylene oxide, and DOBANOL® 91-5 (ex Shell), which is C₉-C₁₁ alcohol ethoxylated with 5 moles of ethylene oxide.

35

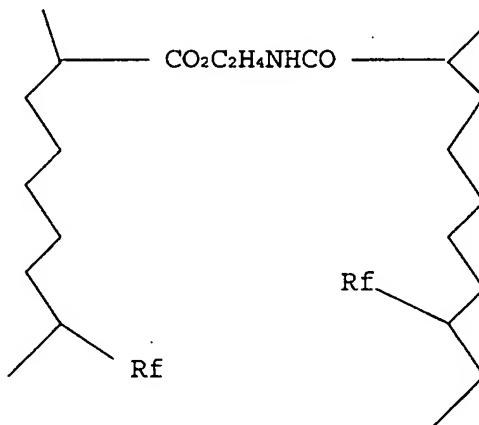
Fluorosurfactants are surfactants in which the hydrophobic segment of the molecule contains fluorine. At least one hydrogen atom in the hydrophobic segment contains fluorine. The hydrophobe can be fully fluorinated (perfluorinated) or 5 partially fluorinated. As with conventional surfactants, fluorosurfactants can be classified into four types: anionic, cationic, amphoteric and nonionic. Their structural features are described in the book "Fluorinated Surfactants - Surfactant Science Series Vol.50" by Eric 10 Kissa, Marcel Dekker Inc., 1994, Chapter 1.

An example of a suitable fluorosurfactant is the material sold by Dow/3M as L13564, of formula (V) :

15

20

25



where Rf is a fluorine containing hydrophobe.

Mixtures of any of the above autophobic hairspray additives 30 may also be used.

Water

Compositions of the present invention include water.

35

Typical water levels for an ethanol-based aerosol fixing spray are from 2 to 10%, usually about 2 to 6% by weight.

5 However, with the advent of legislation concerning the flammability and volatile organic content of hairsprays, it is increasingly desirable to formulate systems with relatively high water content. A particular advantage associated with hairsprays according to the present invention is that they can be formulated with high water 10 content, without prejudice to the autophobic effect.

Hairsprays of the present invention can be formulated with a water content of up to 30%, even 45 to 55% , by weight of the total composition. The upper water content limit is not 15 critical to the present invention, but in general is governed by the tendency of the hairspray formulation to impart a sticky feel to the hair if the level of water is too high.

20 An optimum water level for hairsprays of the present invention is generally from 10 to 25%, e.g. around 15 to 20% by weight of the total composition.

25 Optional Components

A preferred optional component in hairsprays of the invention is a conditioning agent selected from volatile and non-volatile silicone fluids. Volatile silicone fluids are 30 preferably oils chosen from cyclic or linear polydimethyl siloxanes containing from 3 to 9, preferably from 4 to 5 silicon atoms.

35 Cyclomethicone is the most preferred cyclic volatile silicone. Linear volatile silicone oils generally have

viscosities less than about 5 centistokes at 25°C while cyclic fluids typically have viscosities of less than about 10 centistokes.

5 Non-volatile silicone oils useful for the present invention include polyalkyl siloxanes, polyalkylaryl siloxanes and polyether siloxane copolymers. Non-volatile polyalkyl siloxanes useful herein include, for example, polydimethyl siloxanes with viscosities of from 5 to 100,000 centistokes
10 at 25°C. Among the preferred non-volatile silicones are the polydimethyl siloxanes having viscosities from 10 to 400 centistokes at 25°C. These siloxanes are available, for example, from the General Electric Company as SF 1075 methyl phenyl fluid or from Dow Corning as 556 Cosmetic Grade
15 Fluid.

The non-volatile polyalkylaryl siloxane fluids that may be used include, for example, polymethylphenylsiloxanes having viscosities of about 15 to 30,000 centistokes at 25°C.

20 Also includable are minor amounts of other ingredients commonly found in hair care compositions, such as antifoam agents, antioxidants, proteins, preservatives, keratin amino acids, UV inhibitors, fragrances, coloring agents, buffering agents, polyols, and other moisturizing agents. Generally 25 these optional ingredients are included individually at a level of up to about 5% by weight of the total composition.

30 Preferably, compositions of this invention also contain adjuvants suitable for hair care. Generally such ingredients are included individually at a level of up to 2%, preferably up to 1%, by weight of the total composition.

Among suitable hair care adjuvants, are:

(i) natural hair root nutrients, such as amino acids and sugars. Examples of suitable amino acids include arginine, cysteine, glutamine, glutamic acid, isoleucine, leucine, methionine, serine and valine, and/or precursors and derivatives thereof. The amino 5 acids may be added singly, in mixtures, or in the form of peptides, e.g. di- and tripeptides. The amino acids may also be - added in the form of a protein hydrolysate, such as a keratin or collagen hydrolysate. Suitable sugars are glucose, dextrose and fructose. These may be added singly or in the form of, e.g. fruit 10 extracts. A particularly preferred combination of natural hair root nutrients for inclusion in compositions of the invention is isoleucine and glucose. A particularly preferred amino acid nutrient is arginine.

15 (ii) hair fibre benefit agents. Examples are:

- ceramides, for moisturising the fibre and maintaining cuticle integrity. Ceramides are available by extraction from natural sources, or as synthetic ceramides and pseudoceramides. A 20 preferred ceramide is Ceramide II, ex Quest. Mixtures of ceramides may also be suitable, such as Ceramides LS, ex Laboratoires Serobiologiques.

25 The invention will now be further illustrated by the following, non-limiting Example:

EXAMPLE

An illustrative formulation according to the present invention is described below.

5

INGREDIENT	WEIGHT %
Concentrate	
AMPHOMER® ⁽¹⁾	2.80
Aminomethylpropanol	0.46
Perfume	0.15
Dextrose	0.01
Isoleucine	0.01
SILWET® L-7602 ⁽²⁾	0.08
DC345 ⁽³⁾	0.08
Sodium benzoate	0.20
Water	17.00
Alcohol	balance
Propellant	
Hydrocarbon 2.7B	15.00
Dimethyl Ether	30.000

⁽¹⁾ Octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer, ex National Starch.

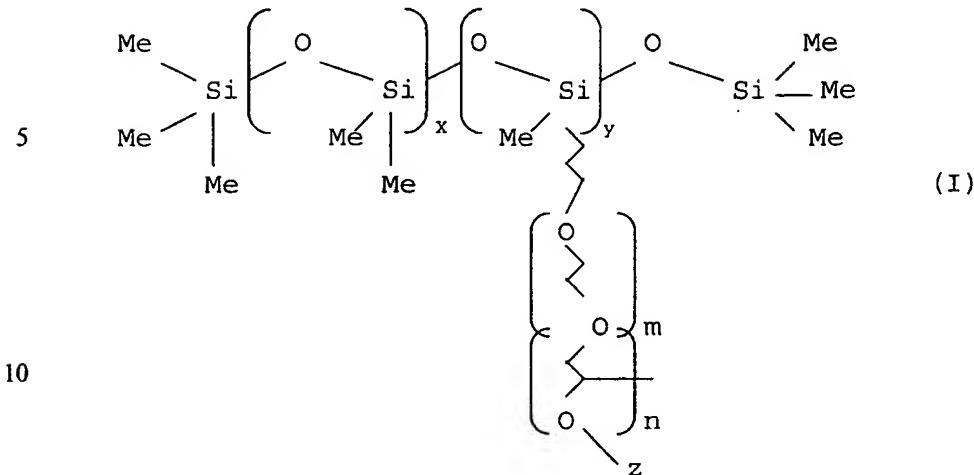
⁽²⁾ Ethoxylated dimethicone copolyol ex OSI Specialities

(3) Cyclomethicone, ex Dow Corning

CLAIMS

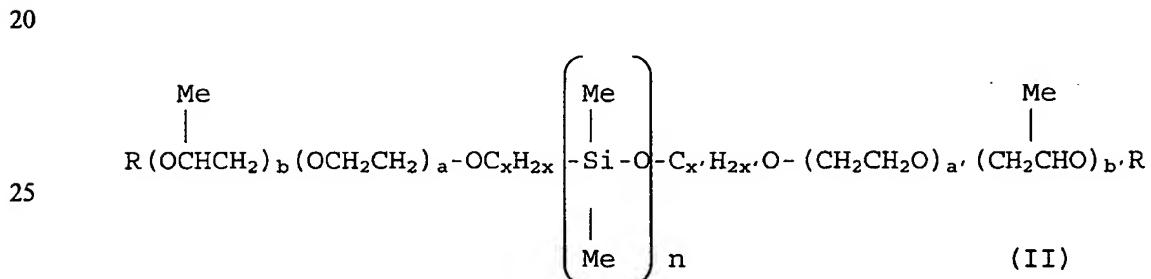
1. A single phase autophobic hairspray composition
5 comprising:
 - a) from 0.5 % to 10 % by weight of a film-forming hairspray resin;
 - 10 b) from 10 to 60% by weight of a propellant including a mixture of at least one hydrocarbon and a di(C₁-C₄ alkyl) ether in a weight ratio from 5:1 to 1:10;
 - c) from 0.01% to 1.0% by weight of an autophobic hairspray additive, being a surfactant or polymer which imparts autophobic behaviour to the hairspray composition, and
 - 15 d) water.
- 20
2. A hairspray composition according to claim 1, in which the film-forming hairspray resin is an amphoteric resin, preferably octylacrylamide/acrylates/butylaminoethyl methacrylate copolymer.
3. A hairspray composition according to claim 1 or 2, in
30 which the autophobic hairspray additive is selected from the group consisting of:

(i) alkyl-pendant silicone copolyols of formula (I):



15 where m and n are integers of from 0 to 50, and x and y are integers chosen to give the copolyol a molecular weight of at least 600. Z is hydrogen or a C1-4 alkyl radical;

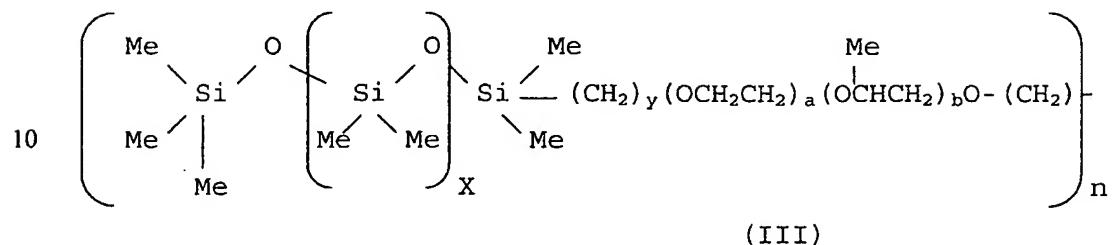
(ii) dimethicone copolyols of formula (II):



30 where n is an integer chosen to give the copolyol a molecular weight of at least 600;
 x and x' are integers of from 1 to 12;

a, a', b, b' are integers of from 0 to 50, and R is hydrogen or a C₁-4 alkyl radical;

5 (iii) polydimethicone copolyols of formula (III):



15

where x and n are integers chosen to give the copolyol a molecular weight of at least 500;
y is an integer of from 1 to 12, and
a and b are integers of from 0 to 50;

20

(iv) alkyl ethoxylates; and

(v) fluorosurfactants.

25

4. A hairspray composition according to claim 3, in which the autophobic hairspray additive is a silicone copolyol of formula (I), preferably an ethoxylated dimethicone copolyol.

30

5. A hairspray composition according to any preceding claim, in which the weight ratio of hydrocarbon and di(C₁-C₄ alkyl) ether is from from 1:1 to 1:4, preferably about 1:2.

35

6. A hairspray composition according to any preceding claim, in which the water content is from 10 to 25%, preferably from 15 to 20% by weight of the total composition.

PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : A61K 7/11		A3	(11) International Publication Number: WO 99/48462 (43) International Publication Date: 30 September 1999 (30.09.99)
(21) International Application Number: PCT/EP99/01632			F-60881 Le Meux (FR). MORETTA, Anthony; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside, L63 3JW (GB).
(22) International Filing Date: 12 March 1999 (12.03.99)			(74) Agent: GRIFFITHS, Sarah, Helen; Unilever PLC, Patent Dept., Colworth House, Shambrook, Bedford MK44 1LQ (GB).
(30) Priority Data: 9806295.3 24 March 1998 (24.03.98) GB			(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, UZ, VN, YU, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG).
(71) Applicant (for AU BB CA CY GB GD GH GM IE IL KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW only): UNILEVER PLC [GB/GB]; Unilever House, Blackfriars, London EC4P 4BQ (GB).			Published <i>With international search report.</i> <i>Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(71) Applicant (for all designated States except AU BB CA CY GB GD GH GM IE IL IN KE LC LK LS MN MW NZ SD SG SL SZ TT UG ZW): UNILEVER N.V. [NL/NL]; Weena 455, NL-3013 AL Rotterdam (NL).			
(71) Applicant (for IN only): HINDUSTAN LEVER LIMITED [IN/IN]; Hindustan Lever House, 165/166 Backbay Reclamation, Mumbai 400 020, Maharashtra (IN).			
(72) Inventors: ASHTON, Melanie, Ruth; Unilever Research Port Sunlight, Quarry Road East, Bebington, Wirral, Merseyside L63 3JW (GB). GRIFFITHS, Llyr, Glyndwr, Elida Fabergé, Usine et Laboratoires de Compiègne, ZI - Boîte postale 139,			(88) Date of publication of the international search report: 16 December 1999 (16.12.99)
(54) Title: AEROSOL HAIRSPRAY COMPOSITION			
(57) Abstract			
A single phase autophobic hairspray composition comprising: a) from 0.5 % to 10 % by weight of a film-forming hairspray resin; b) from 10 to 60 % by weight of a propellant including a mixture of at least one hydrocarbon and a di(C ₁ -C ₄ alkyl) ether in a weight ratio from 5:1 to 1:10; c) from 0.01 % to 1.0 % by weight of an autophobic hairspray additive, being a surfactant or polymer which imparts autophobic behaviour to the hairspray composition, and d) water.			

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TC	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/01632A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 A61K7/11

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 A61K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 97 46213 A (UNILEVER) 11 December 1997 (1997-12-11) page 6, line 23 -page 8, line 32; claims 1-5; examples 1-6 ---	1-6
X	WO 93 03704 A (PROCTER & GAMBLE) 4 March 1993 (1993-03-04) page 9, line 34 - page 10, line 4; page 15, line 14-21; page 19, line 15-25; page 23, line 20 - page 26, line 12; page 28, line 5 - page 29, line 15 claims 1-10 ---	1-6
X	EP 0 590 604 A (AMERCHOL) 6 April 1994 (1994-04-06) page 5, line 42 - line 52; claims 1-10; tables 1,4 ---	1,3,4,6 -/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority, claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

Date of mailing of the international search report

20 October 1999

27/10/1999

Name and mailing address of the ISA
European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Willekens, G

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 99/01632

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 176 898 A (M.E. GOLDBERG ET AL.) 5 January 1993 (1993-01-05) column 2, line 43 - line 67; claims 1-16; examples 1-5 ---	1-6
X	DE 44 21 562 A (GOLDWELL) 21 December 1995 (1995-12-21) page 3, line 17 - line 25; claims 1-8; example 1 ---	1-6
E	WO 99 17711 A (UNILEVER) 15 April 1999 (1999-04-15) the whole document -----	1-6

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 99/01632

Patent document cited in search report	Publication date	Patent family member(s)			Publication date
WO 9746213	A 11-12-1997	US 5840280	A	24-11-1998	
		AU 2776797	A	05-01-1998	
		EP 0907347	A	14-04-1999	
WO 9303704	A 04-03-1993	AU 2502892	A	16-03-1993	
		BR 9206388	A	27-12-1994	
		CA 2115154	A	04-03-1993	
		CN 1071331	A	28-04-1993	
		CZ 9400352	A	13-07-1994	
		EP 0600008	A	08-06-1994	
		FI 940771	A	18-02-1994	
		HU 67488	A	28-04-1995	
		JP 6509807	T	02-11-1994	
		MX 9204802	A	01-04-1993	
		NO 940538	A	14-04-1994	
		NZ 243996	A	27-06-1995	
		PT 100791	A	30-09-1993	
		SK 19294	A	07-12-1994	
EP 590604	A 06-04-1994	US 5413775	A	09-05-1995	
		AU 4864093	A	14-04-1994	
		BR 9303935	A	10-05-1994	
		CA 2107195	A	30-03-1994	
		JP 2899936	B	02-06-1999	
		JP 6207073	A	26-07-1994	
		MX 9305982	A	31-01-1995	
		US 5589157	A	31-12-1996	
US 5176898	A 05-01-1993	AT 131032	T	15-12-1995	
		AU 657832	B	23-03-1995	
		AU 3203393	A	26-08-1993	
		CA 2089049	A,C	22-08-1993	
		DE 69300923	D	18-01-1996	
		DE 69300923	T	25-04-1996	
		DK 557087	T	09-04-1996	
		EP 0557087	A	25-08-1993	
		ES 2079943	T	16-01-1996	
		ZA 9301130	A	20-12-1993	
DE 4421562	A 21-12-1995	AT 157531	T	15-09-1997	
		DE 59500585	D	09-10-1997	
		EP 0688556	A	27-12-1995	
		JP 8034712	A	06-02-1996	
		US 5658552	A	19-08-1997	
WO 9917711	A 15-04-1999	AU 9742098	A	27-04-1999	